4102

Copolymer Composition as a Function of Molecular Weight and the Effect of Conversion on This Relationship

FRANCIS M. MIRABELLA, JR.* and EDWARD M. BARRALL II,**
Institute of Materials Science and Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268, EDMUND F. JORDAN, JR., *Eastern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Philadelphia, Pennsylvania 19118,* and JULIAN F. JOHNSON,† *IBM Research Laboratory, San Jose, California 95193*

Synopsis

The copolymer compositions as a function of molecular weight for three poly(styrene-co-vinyl stearate) copolymers of widely varying conversion were determined. A combined gel permeation chromatography–infrared spectroscopy method was used. Theoretical changes in copolymer composition were calculated using reactivity ratios. Comparison of the calculated and observed changes in copolymer composition as a function of molecular weight showed qualitative agreement. However, the observed changes in composition were significantly larger than those calculated.

INTRODUCTION

In part XXXVI of this series,[1] a rapid technique was described for determining copolymer composition as a function of molecular weight. This method, with some modification, has been used to determine the composition as a function of molecular weight of three poly(styrene-co-vinyl stearate) copolymers described in Table I. The variation of compositional heterogeneity with conversion has been treated theoretically by Skeist.[2] A simplified method of calculation of the Skeist treatment has been reported by Kruse.[3] Little experimental testing of the relationship of compositional heterogeneity and conversion has been reported.

The conversions of the three aforementioned copolymers varied widely. The compositional heterogeneity of these copolymers was compared in order to assess the effect of the differing conversions. Further, the compositional heterogeneity was calculated for each copolymer and the theoretical compared to the observed heterogeneity.

TABLE I[a]

Sample no.	Feed composition, mole-% vinyl stearate	% Conversion[b]	Overall composition, % w/w styrene[c,d]
422-103-1	10	87.3	84.96
422-103-2	20	54.4	81.18
422-103-5	50	20.6	92.72

[a] Data in this table were taken from ref. 4.

[b] All copolymerizations done in bulk at 60°C for 72 hr. Copolymerizations 1 and 2 were run uninterrupted with 0.2 mole-% azobisisobutronitrile (AIBN). Copolymerization 5 was run 24 hr with 0.2 mole-% AIBN and then interrupted, another 0.2 mole-% AIBN added, and continued.

[c] Based on carbon–hydrogen analysis with oxygen obtained by difference.

[d] Residual monomer was extracted from the copolymers with portions (5 to 1 based on polymer) of methanol at the boiling point for 1 hr until an aliquot of methanol failed to produce turbidity when added to water, indicating the absence of monomer. Four or more extractions were done on each copolymer sample.

The experimental apparatus has been described in detail previously.[1] It consisted of a gel permeation chromatograph (built in house) with a 4.0-cc injection loop, five ¼-in., 1-meter columns (1250 Å, 370 Å, 2000 Å, 200 Å, and 1000 Å nominal exclusion limit deactivated porous glass beads), and a Perkin-Elmer (Norwalk, Conn.) 21 infrared spectrometer as a detector. The IR detector was fitted with a refracting beam condenser and a 3-mm pathlength, 50-microliter flow-through cell. Solutions of copolymers were made in tetrachloroethylene (Fisher Scientific Co., technical grade) at a concentration of 15.00 mg/cc by heating just below the boiling point for 5 to 10 min. They were chromatographed, as in the previous work, using 4.0-cc injections for a total sample load of 60 mg, in stop-and-go fashion with infrared spectra being scanned at each syphon dump event over the elution range of the copolymer. Concentrations of each comonomer were obtained by direct calibration by measuring the absorbance of a single peak for each comonomer. Figure 1 shows a GPC curve and a stop-and-go GPC curve, showing the IR spectrum of the 5.0- to 7.0-micron region of one of the 50-microliter fractions taken at a particular syphon dump event, for sample 422-103-1. It was shown that the peak at 5.680 microns (1760 cm^{-1}) was due only to vinyl stearate, the carbonyl stretching vibration. The peak at 6.655 microns (1503 cm^{-1}) was shown to be due only to styrene, an aromatic ring vibration. This was checked by determining a calibration curve (absorbance versus concentration) for poly(vinyl stearate) homopolymer at 5.680 microns (1760 cm^{-1}) and a calibration curve for polystyrene homopolymer at 6.655 microns (1503 cm^{-1}). Then these same calibration curves were redetermined using 50% w/w mixtures of poly(vinyl stearate) and polystyrene homopolymers. The calibration curves were equivalent within experimental error at each wavelength. These data are presented in Figure 2. The calibration curves used were obtained by drawing the best curves, shown as solid lines in Figure 2, through the two sets of data collected at each wavelength.

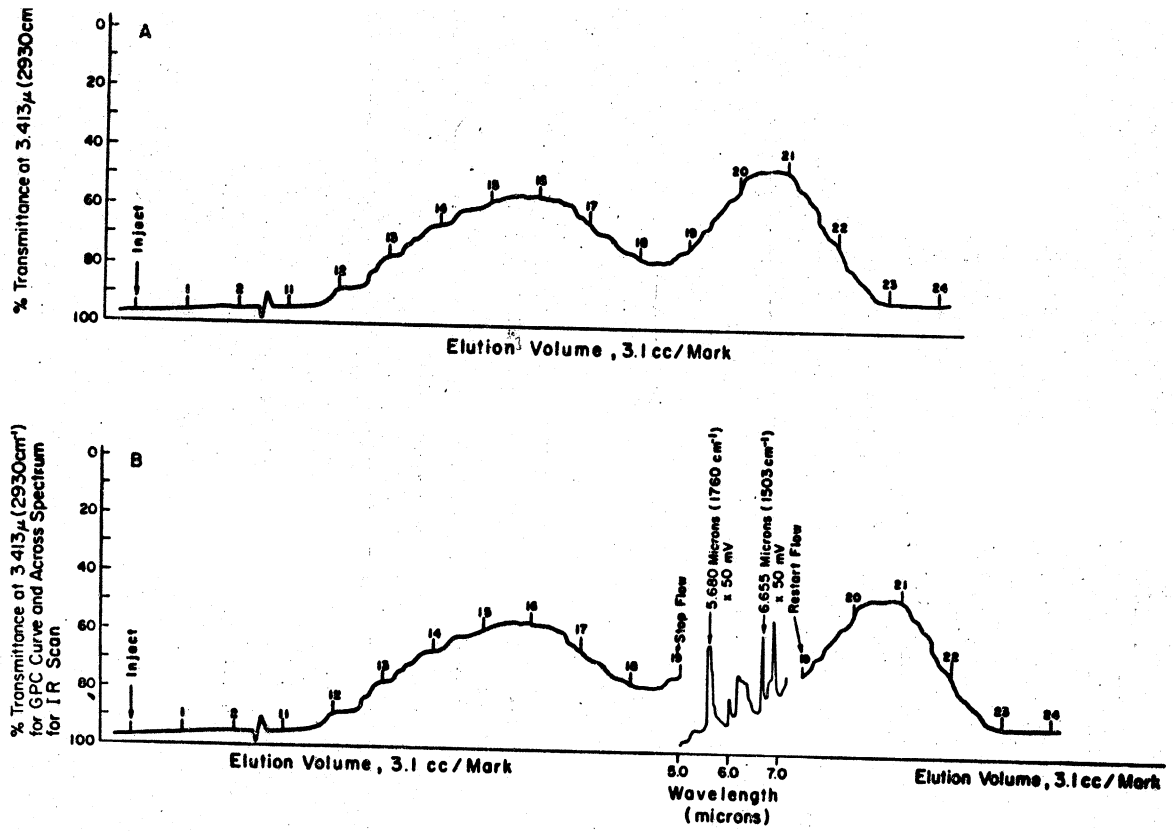

Fig. 1.(A) GPC curve of sample 422-103-1 run on the system described. Injection volume was 4.0 cc; 100 mV scale expansion. (B) Stop flow GPC curve of sample 422-103-1. Same as A, except showing the IR spectrum of the 58.9 cc elution volume fraction.

Elution volumes were converted to "working" molecular weights, as in the previous paper,[1] by using a polystyrene and vinyl stearate calibration curve (Fig. 3).

Vinyl stearate was chosen as the lowest molecular weight standard since it was expected that its elution volume would be representative of the lowest molecular weight species in the copolymers. The extrapolations of the curve in Figure 3 were used to obtain molecular weights for elution volumes outside the range of the standards used.

RESULTS AND DISCUSSION

The composition data for the three poly(styrene-co-vinyl stearate) copolymers are tabulated in terms of syphon dump numbers in Table II. Figure 4 shows a plot of the mean weight per cent styrene in the copolymer versus log "working" molecular weight for the three copolymer samples.

The theory of Skeist[2] as modified by Kruse[3] was used to calculate the theoretical compositional heterogeneity in order to compare this with the observed heterogeneity. The values of the reactivity ratios were $r_1 = 68 \pm 30$ and $r_2 = 0.01 \pm 0.01$, where styrene is monomer 1 and vinyl stearate is mono-

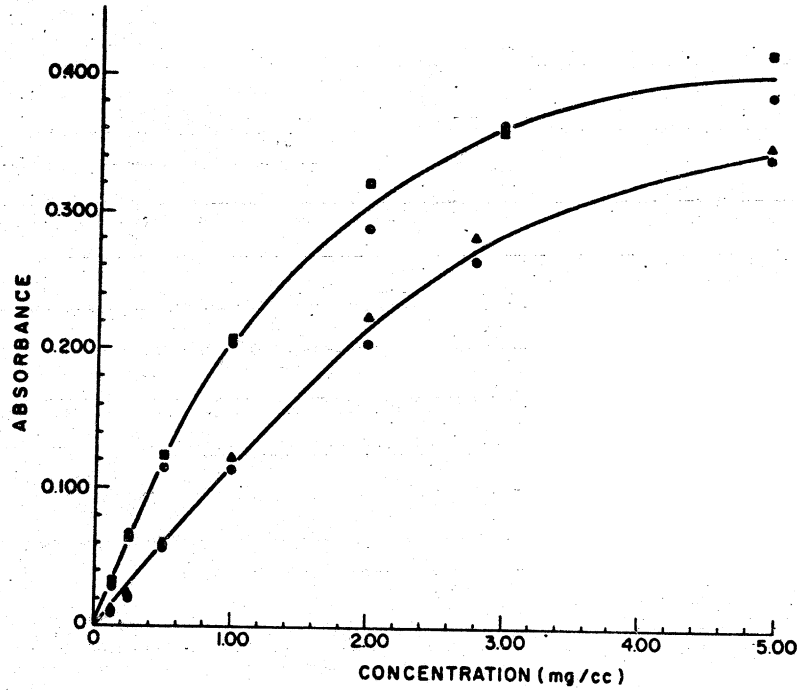

Fig. 2. Calibration data for the determination of vinyl stearate and styrene in poly(styrene-co-vinyl stearate) copolymer: (●) for vinyl stearate from poly(vinyl stearate) homopolymer, absorbance at 5.680 microns (1760 cm^{-1}); (■) for vinyl stearate from poly(vinyl stearate) and polystryene 50% w/w mixture, absorbance at 5.680 microns (1760 cm^{-1}); (▲) for styrene from polystyrene homopolymer, absorbance at 6.655 microns (1503 cm^{-1}); (●) for styrene from poly(vinyl stearate) and polystyrene 50% w/w mixture, absorbance at 6.655 microns (1503 cm^{-1}). The upper curve was used to obtain poly(vinyl stearate) concentrations while the lower curve was used to obtain polystyrene concentrations.

mer 2, as determined for their radical initiated copolymerization at 60°C in bulk.[5,6] Figure 5 shows the calculated compositional change for the three copolymers as weight per cent styrene in the copolymer versus conversion, p.

Table III compares the observed and calculated copolymer compositional changes as a function of degree of conversion. The observed changes in composition agree qualitatively with those predicted from theory in that for the higher-conversion samples (422-103-1 and 422-103-2), the change in composition was larger than for the low-conversion sample (422-103-5). The observed values are significantly different than those predicted for the mea-

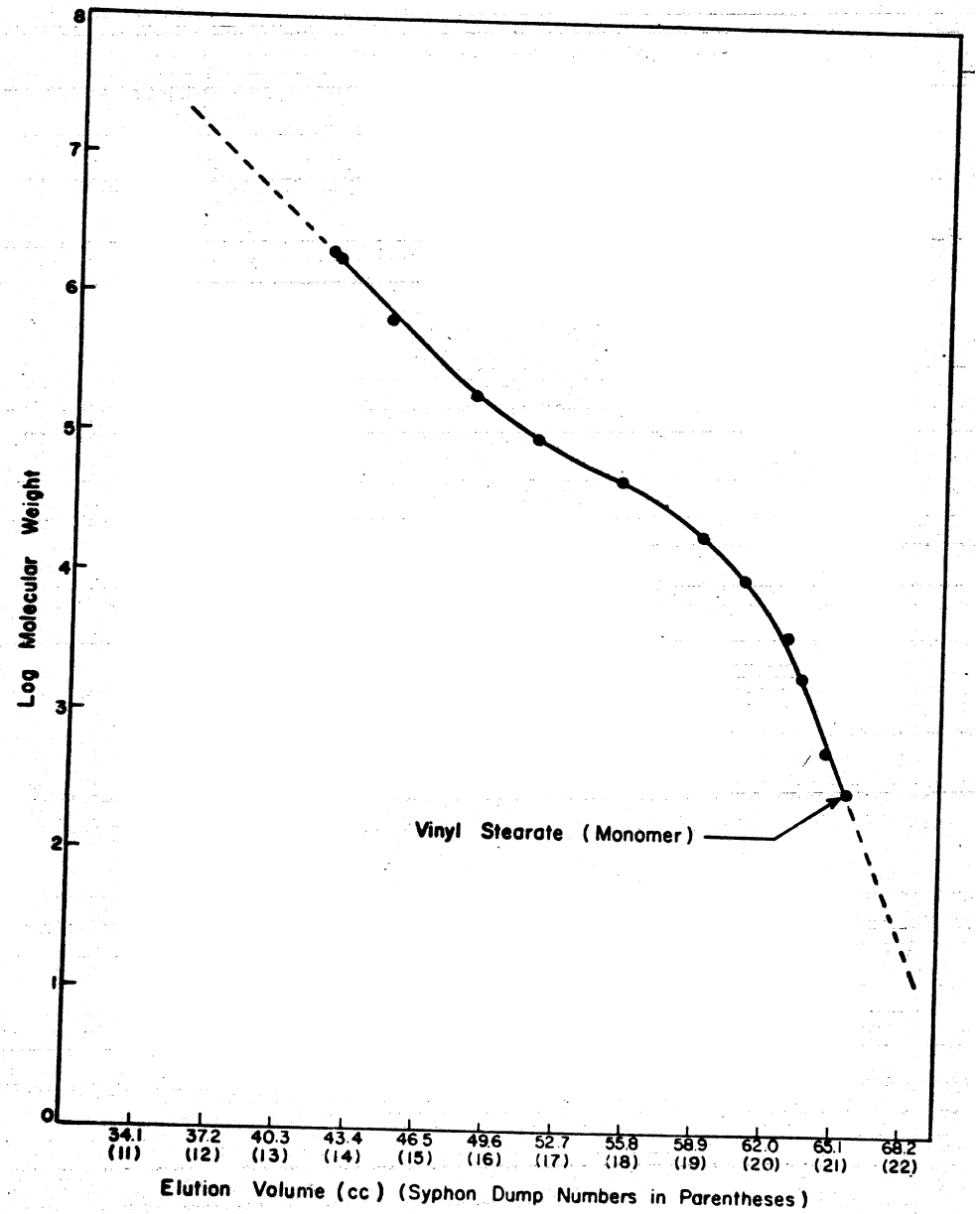

Fig. 3. Calibration curve for GPC system using polystyrene narrow MWD standards (Pressure Chemical Co.) and vinyl stearate monomer. See text for explanation of extrapolations.

TABLE II
Copolymer Composition as a Function of Molecular Weight

Syphon dump no.	Sample 422-103-1 "Working" molecular weight M	log M	Mean weight per cent styrene with average deviation of duplicate runs[a]	Sample 422-103-2 "Working" molecular weight M	log M	Mean weight per cent styrene with average deviation of duplicate runs	Sample 422-103-5 "Working" molecular weight M	log M	Mean weight per cent styrene with average deviation of triplicate runs
12	$1.37(10^7)$	7.14	95.54 ± 0.23	—	—	—	—	—	—
13	$4.20(10^6)$	6.62	97.27 ± 0.19	$4.16(10^6)$	6.62	97.69 ± 0.28	—	—	—
14	$1.35(10^6)$	6.13	97.69 ± 0.20	$1.35(10^6)$	6.13	97.46 ± 0.24	$1.45(10^6)$	6.16	93.72 ± 1.61
15	$4.41(10^5)$	5.64	98.27 ± 0.10	$4.45(10^5)$	5.65	97.74 ± 0.01	$4.88(10^5)$	5.69	92.71 ± 0.16
16	$1.55(10^5)$	5.19	98.69 ± 0.13	$1.57(10^5)$	5.20	98.06 ± 0.00	$1.72(10^5)$	5.24	92.99 ± 0.17
17	$7.50(10^4)$	4.88	98.27 ± 0.25	$7.52(10^4)$	4.88	98.10 ± 0.02	$8.31(10^4)$	4.92	92.64 ± 0.31
18	$4.98(10^4)$	4.70	96.64 ± 0.32	$4.84(10^4)$	4.68	98.21 ± 0.34	$5.51(10^4)$	4.74	90.90 ± 1.10
19	$3.67(10^4)$	4.56	63.84 ± 0.05	$2.82(10^4)$	4.50	83.88 ± 0.27	$2.60(10^4)$	4.41	89.21 ± 0.36
20	$1.53(10^4)$	4.18	13.38 ± 1.94	$1.28(10^4)$	4.11	35.68 ± 0.87	$9.72(10^3)$	3.99	63.15 ± 1.22
21	$1.18(10^3)$	3.07	3.75 ± 0.15	$1.21(10^3)$	3.08	0 ± 0.00	$9.73(10^2)$	2.99	29.85 ± 0.72
22	25.82	1.41	0 ± 0.00	25.82	1.41	0 ± 0.00	25.54	1.41	19.11 ± 1.53

[a] Weight per cent vinyl stearate is the difference totaling 100%.

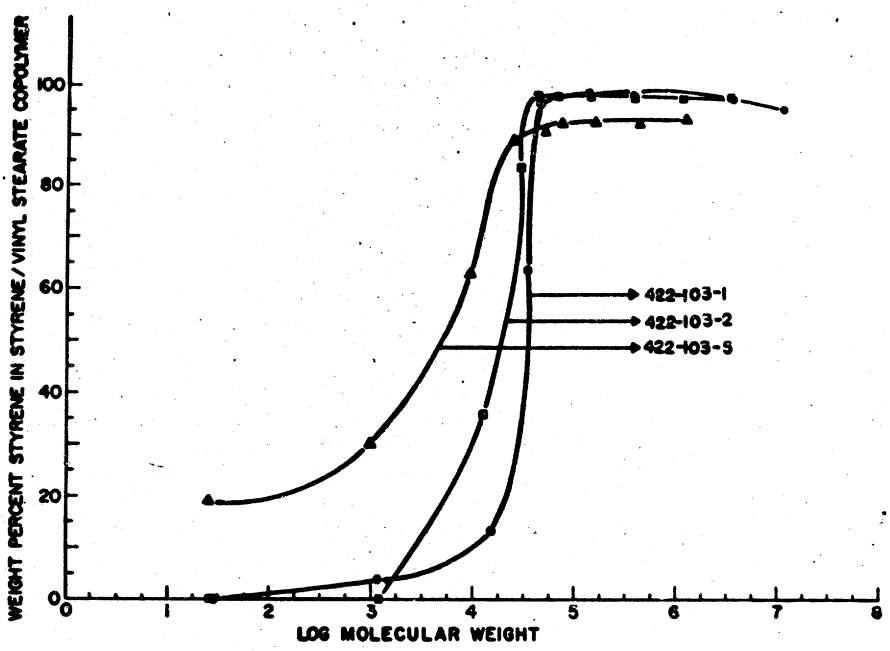

Fig. 4. Mean weight per cent styrene in poly(styrene-co-vinyl stearate) vs. log "working" molecular weight for samples 422-103-1, 422-103-2, and 422-103-5.

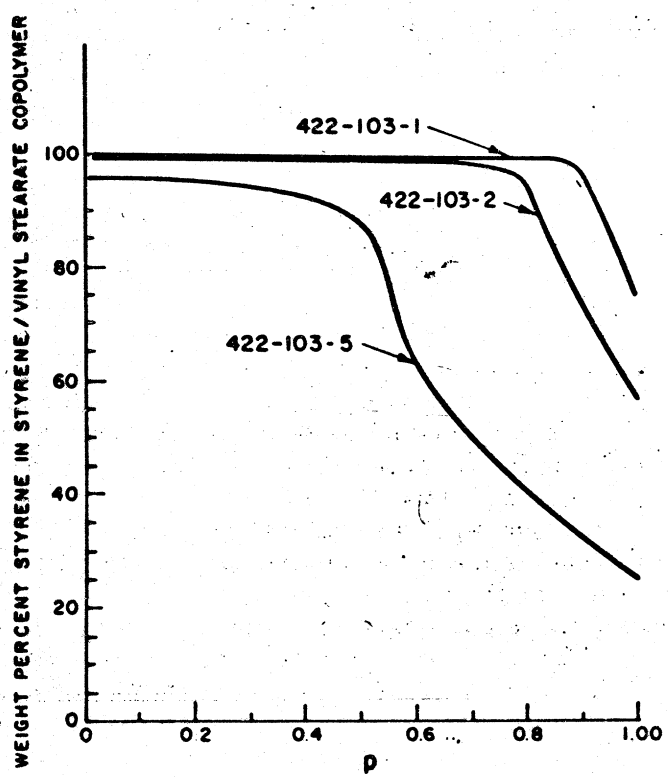

Fig. 5. Theoretical compositional heterogeneity for samples 422-103-1, 422-103-2, and 422-103-5, expressed as weight per cent styrene in the copolymer vs. conversion p.

TABLE III

Comparison of Predicted and Observed Copolymer Compositions for Poly(Styrene-co-Vinyl Stearate)

Styrene in copolymer, wt-%								
	Sample 422-103-1			Sample 422-103-2			Sample 422-103-5	
p_p	Predicted	Range observed	p	Predicted	Range observed	p	Predicted	Range observed
		98.7 to 0.0			98.2 to 0.0			93.7 to 19.1
0	99.6		0	98.9		0	95.5	
0.873[a]	98.2		0.544[a]	98.5		0.206[a]	94.6	
1	75.1		1	57.3		1	25.1	

[a] Experimentally determined conversion, see Table I.

TABLE IV

Comparison of Predicted and Observed Copolymer Compositions for Poly(Vinyl Chloride-co-Vinyl Stearate)

	Vinyl stearate in copolymer, wt-%	
p	Predicted	Range observed
		79.77 to 8.81
0	66.06	
0.7801[a]	66.39	
1	66.66	

[a] Experimentally determined conversion, see ref. 1.

sured degree of conversion; and if the degree of conversion is assumed to be 1, the observed and predicted values are still not in agreement.

Previously reported[1] measurements of copolymer composition as a function of molecular weight have been recalculated using reactivity ratios measured by Marvel and DePierri.[5] Table IV shows that a similar lack of quantitative agreement was found in this case, also.

An essentially invariant copolymer composition was observed for all three copolymers across most of the molecular weight distribution, and it was only at low molecular weights that radical variation in composition was observed. This was similar to the results obtained for poly(vinyl chloride-co-vinyl stearate) previously. The poly(styrene-co-vinyl stearate) copolymers were exhaustively extracted with methanol to remove monomer. Therefore, it appears unlikely that residual vinyl stearate monomer caused the rapid drift toward high-vinyl stearate compositions at low molecular weights. Thus, the material which eluted at 65.49 cc was apparently polymeric and not residual vinyl stearate monomer. Copolymer samples 422-103-1 and 422-103-2 had

bimodal molecular weight distributions, and sample 422-103-5 had a long low molecular weight tail. The rapid change in copolymer composition at low molecular weight may be related to the bimodal molecular weight distributions.

Further experimental investigation is necessary in order to explain the disagreement between the observed and predicted compositional heterogeneity.

A portion of this work was supported by the National Science Foundation through Grant No. MPS 75-01915.

References

1. F. M. Mirabella, Jr., E. M. Barrall II, and J. F. Johnson, *J. Appl. Polym. Sci.*, **19**, 2131 (1975).
2. I. S. Skeist, *J. Amer. Chem. Soc.*, **68**, 1781 (1964).
3. R. L. Kruse, *J. Polym. Sci. B*, **5**, 437 (1967).
4. E. F. Jordan, Jr., private communication, October 4, 1974.
5. C. S. Marvel and W. G. DePierri, *J. Polym. Sci.*, **27**, 39 (1958).
6. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Vol. II, Interscience, New York, p. 271.